

Mg₅C₆₀: A stable two dimensional conducting polymer

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We present a study on the structural, spectroscopic, conducting and magnetic properties of Mg₅C₆₀, a two dimensional (2D) fulleride polymer. The polymer phase is stable up to the exceptionally high temperature of 823 K. Infrared and Raman studies suggest the formation of single bonds between fulleride ions and possibly Mg - C₆₀ covalent bonds. Mg₅C₆₀ is a metal at ambient temperature as shown by electron spin resonance and microwave conductivity measurements. The smooth transition from a metallic to a paramagnetic insulator state below 200 K is attributed to Anderson localization driven by structural disorder.

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I. INTRODUCTION

The unusual physical and structural properties of alkali metal intercalated fulleride polymers have received considerable attention since the discovery in 1994 of the linear AC₆₀ (A=K, Rb, Cs) conducting polymers.¹ Chemical reactions between charged fulleride ions in solids are rather common. The polymer phases usually form spontaneously or under mild pressure from the monomeric crystalline salts. Polymers of C₆₀ⁿ⁻ anions are usually unstable above temperatures of about 400 K. The depolymerization is reversible, in contrast to photopolymerization² and pressure polymerization of neutral C₆₀ (Refs. 3,4). According to quantum chemical calculations,⁵ [2+2] cycloaddition is favored in A_nC₆₀ for low values of n , and configurations with single interfullerene bonds are more stable for $n \geq 3$. In agreement with these expectations, the stable form of AC₆₀⁻ is a cycloaddition polymer,⁶ while single intermolecular bonds occur between C₆₀ⁿ⁻ anions in Na₄C₆₀ (Ref. 7) and Na₂RbC₆₀ (Ref. 8). Single and double bonds can appear simultaneously, as has been recently demonstrated in Li₄C₆₀ (Refs. 9,10) where single bonds connect polyfulleride chains held together by [2+2] cycloaddition bonds.

Fulleride polymers have small electronic bandwidths and large on-site electron repulsion and thus are strongly correlated electron systems. Small differences in the lattice parameters and/or variations in the chain orientation¹¹ can change the ground state profoundly. For example, the linear polymers KC₆₀ and Na₂RbC₆₀ have metallic ground states while RbC₆₀ and CsC₆₀ with the same type of polymer chains but different chain orientations undergo a metal-insulator transition to an antiferromagnetic spin density wave ground state.¹² Electron-electron correlations play an important role in 2D fulleride polymers as well: Na₄C₆₀ is a strongly correlated metal⁷ while Li₄C₆₀ (Ref. 10) is a nonmagnetic insulator.

In this paper, we present a study of the structure and physical properties of the recently synthesized fulleride polymer Mg₅C₆₀. In a previous study of Mg_xC₆₀, a stoichiometric compound¹³ was reported for $x = 4$. In the present work we improved the synthesis and conclude from a series of samples with varying Mg content that the homogeneous phase lies in a range of Mg concentrations between $x = 5$ and $x = 5.5$. Mg₅C₆₀ is the only example of an alkaline earth fulleride polymer. Previous studies of alkaline earth fullerides focused mostly on Ca_xC₆₀ and Ba_xC₆₀ (Refs. 14,15) superconductors which are not polymers. An early study of Mg doped fulleride films reported an insulating behavior for all Mg concentrations¹⁶ in disagreement with our present results.

We find that Mg₅C₆₀ is a 2D polymer which is metallic at high temperature and undergoes a gradual transition to an insulating ground state as the temperature is lowered. It is stable up to the remarkably high temperature of 823 K.

II. EXPERIMENTAL

Samples of Mg_xC₆₀ with nominal concentrations $x = 4$ to 6, in steps of $\Delta x = 0.5$, were prepared by solid state reaction between C₆₀ and pure Mg powders under argon atmosphere in a dry box. The powder mixture was placed in carbon steel containers to avoid reaction between Mg grains and quartz vessels. Mg grain surface activation at 753 K was followed by several annealing steps at temperatures from 653 K to 723 K. To improve the homogeneity of the sample, we used Mg powder with smaller grain sizes than in the previous preparation¹³. Powders were reground before each annealing step.

X-ray powder diffraction was performed using a HUBER G670 Guinier image plate camera in transmission mode and highly monochromatic CuK α ₁ radiation. Infrared spectra were recorded on pressed KBr pellets with

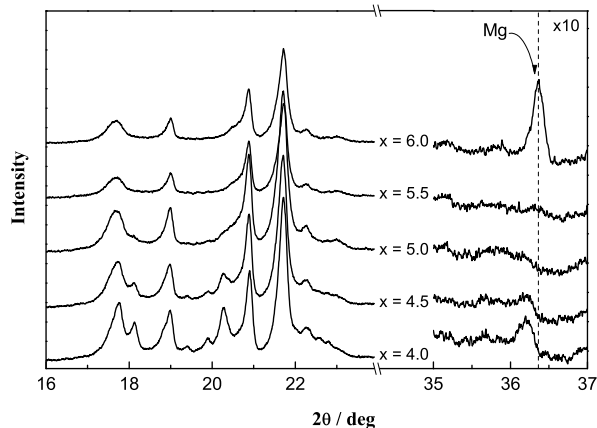


FIG. 1: X-ray powder diffraction data for a series of Mg_xC_{60} polymers, with nominal concentrations x varying from 4.0 to 6.0. Dotted line above 36° corresponds to Mg metal.

a Bruker IFS 28 FTIR spectrometer under dynamic vacuum. Raman spectra were collected using a T64000 Jobin-Yvon spectrometer in triple grating configuration with spectral resolution better than 3 cm^{-1} . The 532 nm line of a frequency-doubled Nd-YAG laser was the excitation source. The diameter of the spot was $100\text{ }\mu\text{m}$ and the nominal irradiance about 150 W/cm^2 , corresponding to $\sim 0.1\text{ mW}$ power on the sample.

Microwave conductivity was measured at 10 GHz on fine Mg_5C_{60} powders mixed with high purity SnO_2 powder to electrically isolate the grains. A 10 GHz copper cylindrical TE011 resonant cavity was used for the cavity perturbation technique conductance measurements^{17,18}. In this method changes in the quality factor are measured using lock-in detection of the frequency modulated response. The sample is placed at the cavity center where the microwave magnetic field is maximum and microwave currents encircle the grains. This geometry is well adapted for fine powders as the microwave electric field is not shielded by depolarization effects.¹⁸ The typical grain size was much less than the microwave penetration depth. The temperature dependence of the conductivity $\sigma(T)$, is proportional to $1/Q - 1/Q_0$. Q and Q_0 , the quality factors of the cavity with and without the sample, respectively, were measured in two separate runs. Q_0 was about 16000 and it changed little with temperature. Ohmic losses of a single spherical grain with radius r and conductivity σ are proportional to $r^5\sigma$. The determination of the absolute value of the conductivity is not possible without a detailed knowledge of the distribution of r .

Electron spin resonance (ESR) spectroscopy was performed at 9 and 225 GHz on samples sealed in quartz tubes under 200 mbar He pressure. At 9 GHz a commercial Bruker ELEXSYS 500 spectrometer was used, the 225 GHz spectra were recorded by a home-built spec-

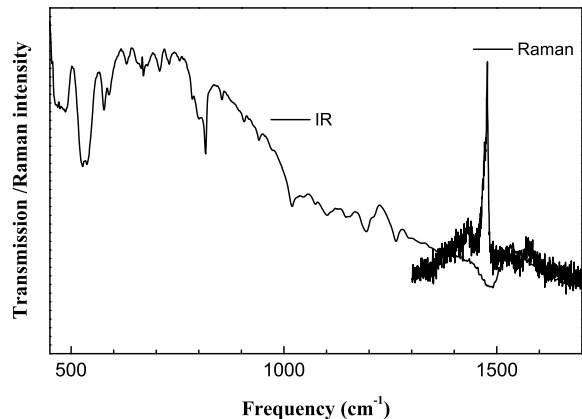


FIG. 2: Infrared and Raman spectra of Mg_5C_{60} .

trometer. The spin susceptibility was obtained by integrating the ESR spectra. MgO doped with 1.5 ppm of Mn^{2+} ions was the ESR intensity reference to obtain the susceptibility between 100 and 300 K. Below 100 K the Mn:MgO ESR saturates and fine orthorhombic polymeric KC_{60} powder (a low conductivity metal with a temperature independent susceptibility) was used as an intensity reference.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Powder diffractograms of a series of Mg_xC_{60} salts (Fig. 1) show that the samples are single-phase for nominal concentration values. The peak above 36° demonstrates that above $x = 5.5$ nominal composition some Mg metal is present. The single-phase material has been indexed in the previous paper¹³ as rhombohedral with lattice parameters $a = b = 9.22\text{ }\text{\AA}$, $c = 25.25\text{ }\text{\AA}$, $\gamma = 120^\circ$. These values indicate the formation of two-dimensional hexagonal C_{60} polymeric sheets in the ab plane. The material belongs to the $R\bar{3}m$ space group. C_{60} molecules are positioned at the fractional coordinates $(0,0,0)$, $(2/3,1/3,1/3)$ and $(1/3,2/3,2/3)$, while the Mg positions are $(0,0,0.23)$ and $(0,0,0.43)$. This structure corresponds to the nominal composition $x = 4$. We regard the magnesium content presented in Fig. 1 more reliable than the previous one¹³, due to the improved synthesis method using fine-powered magnesium metal. The x-ray results also indicate that Mg_5C_{60} is not a line phase but the structure presented here and in Ref. 13 comprises a range of stoichiometries between $x=5$ and 5.5. From the structural data, however, we cannot determine the positions of the additional magnesium ions. A range of alkali concentrations without changes in the structure of the polymer has

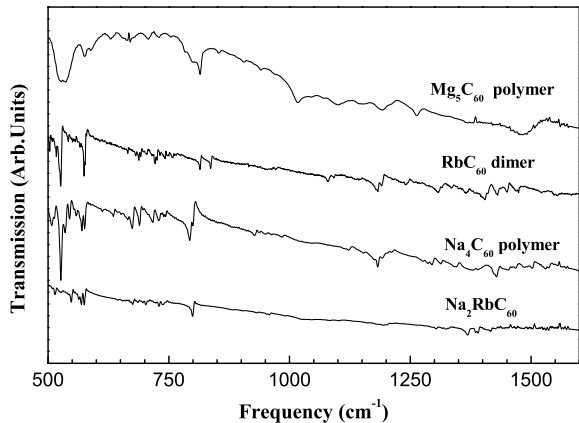


FIG. 3: Comparison of the infrared spectra of various singly bonded fulleride oligo- and polymers.

been observed in Li_xC_{60} ($3 \leq x \leq 5$),¹⁰ with the structural parameters given by a Rietveld fit corresponding to $x = 4$. Subsequent photoemission data on Li_xC_{60} thin films with the same structure proved the charge transfer to be incomplete and constant throughout the homogeneity range.¹⁹

B. Infrared and Raman spectroscopy

The infrared and Raman spectra of Mg_5C_{60} are shown in Fig. 2. The low-frequency part corresponds to a symmetry-reduced C_{60} molecule with the principal T_{1u} modes at 523, 576 and 1193 cm^{-1} , and several new modes, especially in the region between 700-900 cm^{-1} . The lower symmetry confirms polymerization in accordance with x-ray diffraction. The line around 815 cm^{-1} is of particular interest. This line appears in the spectrum of all C_{60} -based polymers^{20,21} where the C_{60} molecules are connected by single bonds (see Fig. 3). We consider the appearance of this characteristic peak in Mg_5C_{60} as proof for single bonds between fulleride ions.

The high-frequency region around the $T_{1u}(4)$ mode shows an unusual pattern, dominated by a broad feature around 1480 cm^{-1} . This feature cannot be explained by a shift in the $T_{1u}(4)$ mode by charge transfer from the Mg atom, neither by polymerization effects, which are both known to reduce the vibrational frequencies.^{22,23} Instead, we assign this peak to the $A_g(2)$ vibrational mode, which is Raman active in undistorted C_{60} . Our assignment is supported by the fact that the peak is also dominant in the Raman spectrum. A similar effect was reported for C_{60} monolayers adsorbed on metal²⁴ and semiconductor surfaces.²⁵ In those systems, an intense infrared absorption above the highest-frequency T_{1u} mode is observed, together with a Raman counterpart,²⁶ attributed to the

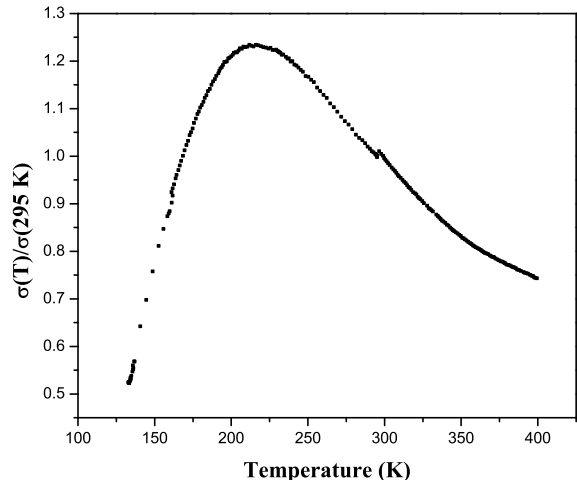


FIG. 4: Microwave conductivity at 10 GHz of Mg_5C_{60} .

$A_g(2)$ mode rendered infrared active by symmetry reduction and amplified by the "vibrational phase relaxation" mechanism.²⁷ Prerequisites for this mechanism are 1. a free-electron continuum, 2. low-frequency vibrational or translational modes which mediate the coupling. According to our ESR and microwave data (see below), conducting electrons are present in Mg_5C_{60} and it is known from Raman spectroscopy of C_{60} photopolymers that intermolecular vibrations appear around 100 cm^{-1} (Ref. 2), thus both criteria are met. In the case of Mg_5C_{60} shown in Fig. 2 the mode is both infrared and Raman-active, but, unlike References 24 and 25, in both cases shifted up by 12 cm^{-1} compared to the 1468 cm^{-1} pristine $A_g(2)$ mode. Such blue shift, albeit smaller, has been observed in C_{60} monolayers adsorbed on platinum,²⁸ where it was explained by covalent bonding to the metal, resulting in electron back transfer from the fullerene to the metal surface. Covalent bonding to at least some of the Mg ions cannot be excluded in the present case either, considering the close values of the Mg ionization potential and the LUMO level of C_{60} . The phenomenon described here warrants further investigation since it was not seen in bulk fulleride salts before.

C. Microwave conductivity and ESR

Both the microwave conductivity and ESR measurements show that Mg_5C_{60} is metallic above room temperature and becomes insulating at low temperature. Fig. 4 displays the temperature dependence of the microwave conductivity of Mg_5C_{60} normalized to 295 K. At high temperatures the conductivity decreases with increasing temperature as it is usual in metals where scattering is due to phonons. The low temperature behavior is dif-

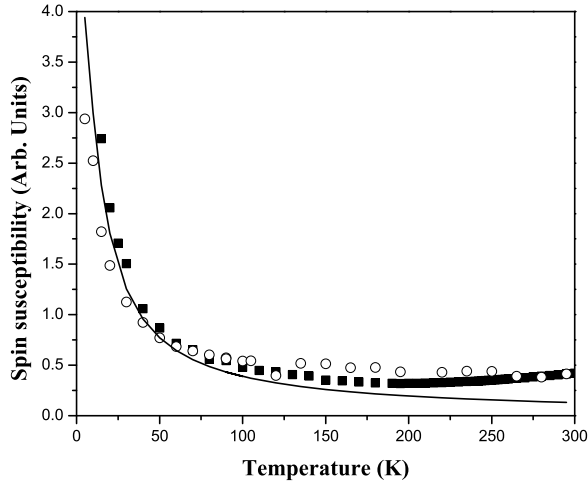


FIG. 5: Temperature dependence of the spin susceptibility of Mg_5C_{60} . 225 GHz ESR measurements (empty circles) are normalized to the 9 GHz ones (squares) at 300 K. The continuous line is the Brillouin function of spin 1/2 in 8.1 T field normalized at 50 K to the 225 GHz measurement.

ferent from usual metals. The conductivity has a broad maximum and decreases below 200 K. This behavior corresponds to a smooth transition between metallic and insulating states.

The ESR spectrum consists of a single Lorentzian line at all temperatures both at 9 and 225 GHz confirming the phase purity of the sample. Phase inhomogeneities usually split the line or at least inhomogeneously broaden it due to differences in the g -factor. If the Mg concentration were inhomogeneous then the high frequency ESR lines would be distorted, especially in the low temperature insulating state where spatial variations are not averaged by spin diffusion.

The change from the low temperature insulating to the high temperature metallic state is observed in the temperature dependence of the spin susceptibility also (Fig. 5). For $T \geq 200$ K the spin susceptibility is almost independent of temperature, as expected for the Pauli susceptibility of a degenerate electron gas. In normal metals the spin susceptibility χ is related to the density of states at the Fermi level $n(E_F)$: $\chi = 1/4g^2\mu_B^2n(E_F)$, where g is the spectroscopic g -factor and μ_B is the Bohr magneton. At lower temperatures a Curie contribution characteristic of a small concentration of localized spins dominates the ESR spectrum (Fig. 5). The change of the temperature dependence of the static susceptibility from Pauli to Curie like is gradual, there is no well defined phase transition. We suggest that the smooth transition to an insulating ground state is due to Anderson localization. At a certain degree of disorder of the lattice the electronic wave functions with an energy below the mobility edge, E_c , become localized.^{29,30} If the Fermi energy

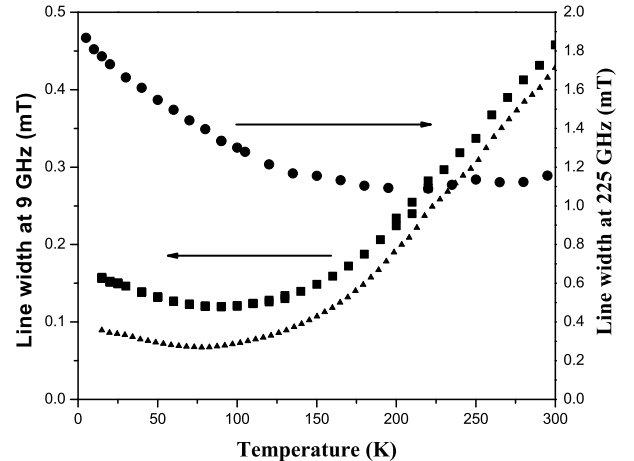


FIG. 6: Temperature dependence of the ESR line width of Mg_5C_{60} at 9 GHz (squares) and 225 GHz (circles). The temperature dependence of the frequency independent component of the line width $a(T)$ is also reported (triangles)

lies below E_c the ground state is insulating. Electrons are delocalized and the behavior is metallic if the temperature is higher than E_c/k_B .

An additional insight into the electron relaxation mechanism is given by the frequency and temperature dependence of the ESR line width. The 9 GHz line is a symmetric Lorentzian with a 4.5 G line width at room temperature. The line broadens inhomogeneously with increasing frequency. The frequency and the temperature dependences of the line width may be separated to give $\Delta H = a(T) + b(T)H$. The frequency independent term $a(T)$ is almost constant below 100 K (see Fig. 6) and increases linearly with temperature as in metals in which the main relaxation mechanism is the electron-phonon interaction.³¹ The term $b(T)$ increases with frequency and with the lowering of temperature. The distortion of the line and the broadening at 225 GHz is due to a partially averaged g -factor anisotropy. We attribute the broadening at $T < 200$ K (see Fig. 6) to the inhomogeneous interaction between paramagnetic defects randomly distributed in the lattice.

We measured a lower limit of the depolymerization temperature by searching for changes in the ESR spectra after annealing at higher temperatures. The sealed Mg_5C_{60} sample was heated at a rate of 10 K/min to each temperature, kept there for 15 minutes, quenched into water and then the 9 GHz ESR spectra were recorded at ambient temperature. We repeated this cycle twice in 25 K steps between 300 and 848 K. We found that treatment up to 823 K leaves the ESR spectrum unchanged. At 848 K the ESR spectrum and the color of the quartz sample holder changed. These changes indicate a reac-

tion of Mg (diffusing out of the sample) with quartz. It is not clear whether without this reaction depolymerization would take place. We conclude that the polymer phase is stable for at least 30 minutes at 823 K.

IV. CONCLUSION

Mg_xC_{60} with $x = 5 - 5.5$ is a single phase, two dimensional fulleride polymer. X-ray diffraction indicates a finite stoichiometry range with the same structure. Vibrational spectroscopy reveals that the Mg-fullerene interaction is more complicated than simple charge transfer, with a possible covalent component. Microwave conductivity shows that Mg_5C_{60} is metallic for $T > 200$ K as confirmed by the temperature dependence of the spin susceptibility and this is the reason for the temperature dependence of the ESR line width in the metallic state.

We attribute the transition from metallic to paramagnetic insulating states below 200 K to a disorder driven Anderson localization. The stability of the polymeric structure of Mg_5C_{60} up to temperatures above 800 K is exceptional, all other polymers of charged fullerenes connected by single or double C-C bonds decompose at much lower temperature.

V. ACKNOWLEDGMENT

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